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#### NEW FORM OF CARBON

This is a continuation-in-part of copending United States Patent Application having Serial Number 575,254 that was filed on August 30, 1990.

# BACKGROUND OF THE INVENTION

This invention relates to new forms of carbon as well as methods for the production and recovery thereof from carbon sources.

In 1985, Kroto et al. postulated the existence of a highly stable molecule composed of 60 carbon atoms based solely on mass spectroscopic analysis of vaporized graphite (H.W. Kroto, et al., Nature, Vol. 318, 162, 14 November 1985). More specifically, all that was observed was a peak in the mass spectra of said carbon vapor. However, Kroto et al. did not isolate any of said compound.

A model for this compound was proposed in which 60 carbon atoms are placed at the vertices of a truncated icosahedron forming a perfect "soccerball" structure. Subsequent thereto, many publications have strengthened the evidence for the existence of this molecule. The 60 carbon atom compound (hereinafter C<sub>60</sub>) was presumably produced in situ for the spectroscopic determination reported in these publications. Yet, to date, no one has been successful in verifying the existence of this molecule since no one has been successful in isolating the molecule in measurable amounts. Thus, no processes for producing recoverable amounts of this new compound have been described to the present time.

In the aforesaid publication by Kroto, et al., the authors proposed many uses for the new substance,  $C_{60}$  if it could be produced in quantity such as  $C_{60}$  transition metal compounds, e.g.,  $C_{60}$ Fe; or halogenated

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species like  $C_{60}F_{60}$  which might be a super lubricant; molecules including oxygen and lanthanum in the  $C_{60}$  interior;  $C_{60}$  would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry; and  $C_{60}$  being especially stable and symmetrical provides possible catalyst and/or intermediate in modelling prebiotic chemistry.

Another form of carbon containing 70 carbon atoms  $(C_{70})$  has also been postulated (Kroto, Chemistry in Britain, 40-45 (1990), Kroto, Science, 1139-1145 (1988)). Like the  $(C_{60})$  to date, no one has been successful in verifying the existence of the  $C_{70}$ . Heretofore, no one has been successful in obtaining the molecule in any appreciable amounts.

## 15 SUMMARY OF THE INVENTION

A process has now been developed for the production of recoverable amounts of  $C_{60}$  and  $C_{70}$ . The present new process is accomplished by evaporating carbon rods in an atmosphere of an inert quenching gas maintained at reduced pressure in a reactor therefor. This process produces a sooty carbon product which is graphitic carbon including a few percent of  $C_{60}$  and low levels of  $C_{70}$  which are recoverable from the product. However, an increase in the fraction of  $C_{70}$  molecules can be produced if the pressure is raised to greater than atmospheric pressures.

The recovery process is preferably accomplished by selective extraction of  $c_{60}$  and  $c_{70}$  with non-polar organic solvents from the sooty graphitic carbon.

The processes of the present invention produces  $c_{60}$  and  $c_{70}$  in recoverable amounts and permits realization of the proposed uses described hereinbefore.

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#### DESCRIPTION OF THE FIGURES

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Fig. 1: MIcrograph of typical crystals of the 98%  $C_{60}$ , 2%  $C_{70}$  material showing thin platelets, rods and stars of hexagonal symmetry.

Fig. 2: X-ray diffraction of a microcrystalline powder of the 98% C<sub>60</sub>, 2% C<sub>70</sub> solid material. Inset at upper left is a single crystal electron diffraction pattern indexed with Miller indices compatible with the X-ray pattern, taken on a thin platelet as in Figure 1 with the electron beam perpendicular to the flat face.

Fig. 3: Infrared absorption spectrum of an approximately 2 micrometer thick coating of the 98%  $C_{60}$ , 2%  $C_{70}$  material on a silicon substrate, referenced to a clean silicon substrate. Absorption is given as optical density =  $\log_{10}$  1/T, where T is transmission. Apparent negative absorptions are due to the coating acting in part as a non-reflecting layer.

Fig. 4: Visible-ultraviolet absorption spectrum of an approximately 0.1 micrometer thick coating of the 98%  $C_{60}$ , 2%  $C_{70}$  material on quartz. Shown at the bottom are positions and relative oscillator strengths for allowed transitions calculated for the  $C_{60}$  molecule by Larsson, et al.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The first step in the production of C<sub>60</sub> and C<sub>70</sub> molecules is vaporizing carbon from any source containing carbon in its various forms, e.g., graphite, amorphous and glassy carbon. It is preferred that this vaporization takes place in an evacuated reactor (e.g., a bell jar). The carbon is vaporized by heating in the presence of an inert quenching gas. The carbon vapor is nucleated in the presence of the inert quenching gas to form smoke particles.

The inert quenching gas can be any of the usual inert gases such as the noble gas. Argon and helium are preferred, the latter being most preferred. Other inert gases commonly employed to provide a non-reactive atmosphere can also be used as quenching gas.

The amount of C<sub>60</sub> and C<sub>70</sub> produced from this carbon source is dependent upon the pressure of the quenching gas. At lower pressures relatively pure C<sub>60</sub> molecules can be produced in high yield with minor concentrations of C<sub>70</sub>. For the production of predominantly C<sub>60</sub> molecules, the pressure at which the quenching gas is maintained should be subatmospheric and preferably about 50-400 torr. Especially preferred is a pressure of approximately 100 torr. The use of any lower pressure may result in reduced yield of C<sub>60</sub>.

However, as the pressure is raised, the ratio of  $C_{70}\colon C_{60}$  is also increased.

If the pressure is increased to at least two atmospheres, the greatest percentage of  $C_{70}$  product is formed. Theoretically, the pressure can be raised to any level just below the point where the reactor would

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explode from the increased pressure. However, at the higher pressures, the yield of the overall product ( $C_{60}$  and  $C_{70}$ ) is reduced even though the ratio of  $C_{70}$ : $C_{60}$  is also increased. Therefore, as a practical consideration, the pressure of the quenching gas should not be greater than 10 atmospheres. The preferred pressure for maximizing the amount of  $C_{70}$  produced is 2-3 atmospheres.

The produced quenched vapor of carbon, i.e., the smoked particles coats the internal surface of the reactor and of collecting substrates as black soot. These collecting surfaces are inert to the vaporized carbon. They can be transparent and/or coated with an inert metal. Examples include glass, or gold coated glass surfaces and the like. These collecting surfaces are located in the reactor in the path of the carbon smoke. The black coating can be removed by any suitable means, e.g., by scraping the solids from the coated surfaces. The  $C_{60}$  and  $C_{70}$  molecules can be removed from this collected quenched product by contacting said quenched product with an extracting solvent. words, the black soot is placed in a container containing the extracting solvent, or the extracting solvent is poured onto the black soot placed in a container. either case, the  $\mathrm{C}_{60}$  and  $\mathrm{C}_{70}$  molcules become dissolved in the solvent, while the remainder of the black soot remains insoluble. The insoluble material is separated from the solution containing the  $C_{60}$  and  $C_{70}$  molecules, e.g., by decanting, or by filtration, and the like.

Suitable solvents include non-polar organic solvents, such as the alkanes containing 5-10 carbon atoms (e.g. pentanes, hexanes, heptanes, octanes), benzene and alkyl-benzenes (e.g. toluene, xylene), carbon disulfide, carbon tetrachloride, naphtha,1,1,1-

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trichloroethane, and the like. Simple solubility
determinations using classical laboratory methods will
permit selection of other suitable solvents. The
preferred solvents are carbon disulfide, benzene, carbon
tetrachloride and toluene. Especially preferred are
benzene, carbon tetrachloride and carbon disulfide.

The product obtained contains a mixture of  $C_{60}$  and  $C_{70}$ . As described hereinabove, the amounts of  $C_{60}$  and  $C_{70}$  present is dependent upon the pressure used. If subatmospheric pressures are used, such as 50-400 torr, the product is predominatly pure  $C_{60}$  with a minor amount of  $C_{70}$  present. Thus, when the collected product is dispersed in the extracting solvent, the product obtained is a mixture of  $C_{60}$  and  $C_{70}$ . For example, when the pressure is 100 torr, the product formed is about 98%  $C_{60}$  and about 2%  $C_{70}$ . This product can be separated from the organic solvent solution by standard methods as by evaporation of the solvent or by dilution of the solvent solution with a non-solvent for  $C_{60}$ . The product can be crystallized by careful evaporation of the organic solvent or by sublimation procedures.

In a preferred embodiment of producing C<sub>60</sub> and C<sub>70</sub>, pure graphite rods are vaporized by passing high electrical current (either dc or ac) through narrowed tips of graphite rods. Electron beam, laser and RF heating can be used in lieu of electrical heating. This is done in a reactor (such as a bell jar) that has been evacuated, purged and filled with inert gas at or preferably below atmospheric pressure, e.g., pressures ranging from about 50 to about 400 torr. and even higher. The graphite rods are typically 1/4 inch in diameter with

about 1 cm length of one rod reduced in diameter to about 5 mm. The electrical heating vaporizes the constricted tip of the graphite rod producing a high density vapor of carbon, which quickly condenses into a smoke consisting of very fine particles (of the order of 0.1 microns) of graphitic carbon with an admixture of a few percent of the desired C<sub>60</sub> molecule. At this point in the process there is a heavy black coating on collecting substrates and/or on the walls of the chamber which can be easily scraped off for the recovery step.

For recovery, the scoty product is treated with benzene to provide a brownish-red solution. After separation of the undissolved graphitic carbon, the benzene solution is evaporated to obtain microcrystalline product. Alternatively, the product can be sublimed from the sooty carbon at 300° to 400°C, and the sublimation product obtained by condensation on a conventional substrate.

When the pressure of inert quenching gas is 100 torr, the product formed is 98%  $C_{60}$  and 2%  $C_{70}$ . This product, as obtained from the solvent extract of the sooty graphitic carbon, is a dark brown to black crystalline material. When obtained by sublimination in vacuum or inert atmosphere, the product is obtained as a brown to gray coating depending on thickness.

On analysis by mass spectroscopy, the spectrum clearly shows a strong peak at mass 720 amu (i.e., the mass of  $C_{60}$ ) and a clean peak at 840 amu (i.e., the mass of  $C_{70}$ ). Significant differences in the spectra occur only in the abundances in the mass domain lower than 300 amu. Most of these differences seem to originate from the different ionization techniques in the mass spectrometer and from the different kinds of sample desorption. So far, the cleanest mass spectra have been

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obtained when the material was evaporated and ionized in the vapor phase by electrons. In such spectra the mass range above 40 amu is dominated by the Coo mass along with its expected isotope lines. The only other large mass found in any abundance corresponds to Coo, with a ratio of Coo to Coo of about .02.

Studies by optical microscopy of the C<sub>60</sub>
material which is left after evaporating the benzene
solution show a variety of what appear to be crystals -
10 mainly rods, platelets, and star-like flakes. Figure 1
shows a micro-photograph of such a crystal assemblage.
All crystals tend to exhibit six-fold symmetry. In
transmitted light they appear red to brown in color; in
reflected light the larger crystals have a metallic
appearance, whereas the platelets show interference
colors consistent with an index of refraction of about 2.

The platelets can be rather thin and thus are ideally suited for electron diffraction studies in an electron microscope. (See the insert in Figure 2).

In order to determine if the C<sub>60</sub> molecules form a regular lattice electron, x-ray diffraction studies on the individual crystals and on the powder were carried out. A typical X-ray diffraction pattern of the purified C<sub>60</sub> powder is shown in Figure 2. To aid in comparing the electron diffraction results with the X-ray results the electron diffraction pattern is inserted into the corner of Figure 2. From the hexagonal array of diffraction spots indexed as shown in the Figure, a d-spacing of 8.7 A was deduced corresponding to the (100) reciprocal lattice vector of a hexagonal lattice. The most obvious correspondence between the two types of diffraction is between the 5.01 A peak of the X-ray pattern and the

(100) spot of the electron diffraction pattern, which gives a spacing of about 5.0 Å. Assuming that the C<sub>60</sub> molecules are behaving approximately as spheres stacked in a hexagonal close packed lattice with a c/a ratio of 1.633, d-spacings can be calculated. The results are shown in Table I.

Table I: X-Ray Diffraction Results and Assignments For a Hexagonal Lattice Using  $a = 10.02 \ \%$ ,  $c = 16.36 \ \%$ 

$$\frac{1}{d^2} = \frac{4 (h^2 + hk - k^2)}{3 (a^2)} + \frac{2}{c^2}$$

15 	Measured 20 (degrees	Measured d-spacing	Calculated d-spacing	Assignment (hkl)
	10.2 shoulder	8.7	8.68	
20 25	10.81	8.18	8.18	(100)
			7.67	(002)
	17.69	5.01	5.01	(101)
	20.73	4.28	_	(110)
	21.63	4.11	4.27	(112)
	28.1	3.18	4.09	(004)
	30.8	2.90	3.17	(114)
	32.7		2.89	(300)
	J2./	2.74	2.73	(006)

The values derived from this interpretation are a = 20.02 Å and c = 16.36 Å. The nearest neighbor distance is thus 10.02 Å. For such a crystal structure the density is calculated to be 1.678  $g/cm^3$ , which is consistent with a value of 1.65 +/- .05 determined by suspending crystal samples in aqueous GaCl<sub>3</sub> solutions of

known densities. Although the agreement shown in Table 1 is good, the absence of the characteristically strong (101) diffraction in hcp and the broad continuum in certain regions suggest a less than perfect crystalline order. Furthermore, X-ray diffraction patterns obtained on carefully grown crystals up to 500 micrometers in size with well developed faces yielded no clear spot pattern (in contrast to the electron diffraction pattern on micron-size crystals). It thus appears that these larger crystals do not exhibit long range periodic order in all directions.

A likely explanation for the unusual diffraction lies in the disordered stacking arrangement of the molecules in planes normal to the c-axis. It is well known that the position taken by spheres in the 15 third layer of stacking determines which of the close-packed structures occurs, the stacking arrangement in fcc being ABCABC while that in hop is ABABAB. If the stacking sequence varies, the X-ray lines due to certain planes will be broadened by the disorder while other 20 lines will remain sharp. Such disordered crystalline behavior was observed long ago in the close packed structure of cobalt, where X-ray diffraction lines such as (101), (102) and (202) were found to be substantially broadened due to the stacking disorder. Reflections from 25 planes such as (002) remain sharp since these planes have identical spacings in both fcc and hcp structures. A general expression for which peaks are broadened by this kind of disorder have been given in terms of Miller indices (h,k,l) as h - k = 3t  $\pm$  1, 1  $\neq$  0, where t is an 30 integer. None of these broadened reflections are apparent in the X-ray pattern of Figure 2. This may explain the weakness of the characteristically strong

(101) peak. Whether or not this stacking disorder is related to the presence of the possibly elongated  $C_{70}$ molecules is yet to be determined.

In small crystals at least, the  ${\rm C_{60}}$  molecules appear to be assembling themselves into a somewhat ordcred array as though they are effectively spherical, which is entirely consistent with the soccer ball hypothesis for their structure. The additional diameter over the calculated 7.1  $ilde{\mathsf{A}}$  value for the carbon cage itself must represent the effective van der Waals diameter set by the repulsion of the pi electron clouds extending outward from each carbon atom. Scanning tunnelling spectroscopy of the  $C_{60}$  molecules clearly shows the spherical nature of the  $C_{\text{60}}$  molecules.

Some scanning tunnelling microscope images of a 15 carbon sample prepared in accordance with the procedure described hereinabove at pressures of helium at 100 torr show a spherical molecule of twice the diameter of the  $C_{60}$  molecules. This is evidence of the existence of a caged molecule containing 240 carbon atoms or a  $C_{240}$ molecule.

Samples were prepared for spectroscopy by subliming pure material onto transparent substrates for transmission measurements. Depending on the pressure of helium in the sublimination chamber, the nature of the coatings can range from uniform films (at high vacuum) to coatings of  $c_{60}$  smoke (i.e., sub-micron microcrystalline particles of solid  $C_{60}$ ) with the particle size depending to some extent on the pressure.

Figure 3 shows the transmission spectrum of an 30 approximately 2 micrometer thick  $C_{60}$  coating on a silicon substrate. The infrared bands show the four most intense lines at 1429, 1183, 577, and 528  $cm^{-1}$ , with no

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underlying continuum remaining from the soot. In early tries at purifying C<sub>60</sub> material, the infrared spectrum showed a strong band in the vicinity of 3.0 micrometers, which is characteristic of a CH stretching mode. After much effort, this contaminant was successfully removed by washing the soot with ether and using distilled benzene in the extraction. The spectrum in Figure 3 was obtained when the material cleaned in such a manner was sublimed under vacuum onto the substrate. The spectrum shows very little indication of CH impurities.

The presence of only four strong bands is what is expected for the free, truncated icosahedral molecule with its unusually high symmetry. Also present are a number of other weak infrared lines which may be due to other causes, among which may be absorption by the C70 molecule or symmetry breaking produced, for example, by isotopes other than  $c^{12}$  in the  $c_{60}$  molecule or by mutual interaction of the C<sub>60</sub> molecules in the solid. Noteworthy, are weaker features at about 2330 and 2190 cm<sup>-1</sup> which are located in the near vicinity of the free CO2 and CO stretching modes. This may imply some attachment of CO2 or CO to a small fraction of the total number of  $C_{60}$  molecules. Another noteworthy effect can be observed in the feature at 675 cm<sup>-1</sup>, which is weak in the thin film samples but almost as strong as the four main features in the crystals. This vibrational mode may be of solid state rather than molecular origin.

Figure 4 shows an absorption spectrum taken on a uniform film coated onto a quartz glass substrate. The ultraviolet features are no longer obscured by the graphitic carbon background as in our previous spectra. Broad peaks at 216, 264 and 339 nm dominate the spectra. Weaker structures show up in the visible, including a

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plateau with ends at about 460 and 500 nm and a very weak peak near 625 nm. At the bottom of Figure 4 are snown positions and relative oscillator strengths taken from Larsson, et al. (Chem. Phys. Lett. 137, 501-504)

calculated for the C<sub>60</sub> molecule. This reference also shows a variety of forbidden bands with the lowest energy ones in the vicinity of 500 nm. There seems to be a rough correspondence between the present measurements on thin films and the allowed transitions predicted for the molecule. There was no band at 386 nm in our films of C<sub>60</sub>, a disclosed by Heath, et al. (1. Chem. Days 27)

10 molecule. There was no band at 386 nm in our films of C<sub>60</sub>, a disclosed by Heath, et al. (J. Chem. Phys. <u>87</u>, 4236-4238 (1987)) using a laser depletion spectroscopy method and attributed to the C<sub>60</sub> molecule. Quite similar spectra to that in Figure 4 have been recorded for

microcrystalline coatings deposited at helium pressures of 100 torr, for example. The peaks occur at the slightly shifted positions of 219, 268, and 345 nm.

The C<sub>70</sub> molecule is larger than the C<sub>60</sub> molecule. The C<sub>70</sub> molecule shows a molecular ion peak at 840 amu. Furthermore, a noticeable peak in the ultraviolet spectrum of the C<sub>70</sub> molecule taken on a uniform film coated onto a guartz glass substrate is exhibited at about 216 nm. This is a broad peak. Suprisingly, it appears that the C<sub>70</sub> molecule is more stable than C<sub>60</sub>.

Thus, using the procedures described hereinabove, at quenching pressures of less than 1 atmospheric pressure and especially at pressures of 50-400 torr, a product is produced which is predominantly  $C_{60}$  and cantains minor amounts of  $C_{70}$ . The  $C_{60}$  product can be used or can be further purified.

Further purification and separation of  ${\rm C_{60}}$  and  ${\rm C_{70}}$  can be made by many conventional techniques known to

one skilled in the art; e.g., fractional crystallization, column chromatography, capillary electrophoresis, HPLC, preparative thin-layer chromatography, and the like.

Because the molecular figuration of  $C_{60}$  and  $C_{70}$  are different, the attractive intermolecular forces are different which allows for the two molecules to be readily separated.

Furthermore, the solubility of  $C_{60}$  and  $C_{70}$  in pure solvents and mixed solvents are also different from each other, which also makes the two compounds separable by using conventional techniques known to one skilled in the art, such as crystallization, extraction, and the like.

For example, pure  $C_{60}$  and pure  $C_{70}$  molecules can be isolated as follows. The black sooty mixture of  $c_{60}$  and  $c_{70}$  which is produced according to the procedure described hereinabove is placed in the extracting solvent, such as benzene. The insoluble residue is removed and the resulting benzene solution containing  $C_{60}$ and  ${\rm C}_{70}$  molecules is concentrated. The  ${\rm C}_{60}$  and  ${\rm C}_{70}$ solution is added to a packed column with an adsorbent, such as alumina. The column is eluted with an eluent such as benzene or a mixture of benzene and toluene. Various fractions of set volume e.g., 10 mL, are collected. The eluent i.e., the solvent is removed from each fraction such as by evaporation to dryness. The fractions with product will contain microcrystals, the identity of which can be confirmed by spectroscopy, e.g., mass spectroscopy.

Thus, the process of the present invention can produce a product which is predominantly C<sub>60</sub>, which, if desired, can be further purified by the purification and separation techniques described hereinabove.

Furthermore, the present invention contemplates two different variations of the procedure described hereinabove to make C<sub>70</sub> molcules. First, if subatmospheric pressures of quenching gases are used in the initial step, small amounts of C<sub>70</sub> are produced, which can be separated from the C<sub>60</sub> molecules using the purification techniques described hereinabove. However, if the pressure of the quenching gas is raised to at least 2 atmospheres, after separation and purification, a greater percentage of substantially pure C<sub>70</sub> would be produced from each vaporization of carbon.

The present new products, Coo, Coo, or mixtures thereof have the similar utilities as graphite. However, they are particularly valuable for forming products of a higher order of stability than those formed from 15 graphitic carbon, and can be processed into formed or molded products such as  $C_{60}$  fibers,  $C_{70}$  fibers, or mixtures thereof using standard processing techniques. In this regard, free-flowing, particulate  $C_{60}$  and  $C_{70}$  are of special value particularly for use in producing molded products, especially those extended in at least one direction.  $C_{60}$ , and  $C_{70}$  are also useful for producing a low temperature C<sub>60</sub> vapor (300°-400°C.) and C<sub>70</sub> vapor of the respective molecules to produce low temperature atomic and molecular beams of carbon which is not now 25 possible using graphite as the carbon source. Further, the synthesis of compounds such as  $C_{60}^{\rm H}{}_{60}$  and  $C_{60}^{\rm F}{}_{60}$  can be accomplished by introducing hydrogen and fluorine, respectively, into a reactor containing C60 vapor. Furthermore, the  $C_{60}$  product and the  $C_{70}$  product may be used as an industrial paint pigment or as a lubricant. Moreover, since the  $C_{60}$  and  $C_{70}$  molecule are hollow, they could be used for binding and/or storing molecules e.g., toxic material.

EXAMPLE 1

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 ${\rm C}_{60}$ -containing carbon dust was produced in a conventional bell-jar carbon evaporator which was first evacuated to  $10^{-4}$  torr by either an oil diffusion pump or a turbo pump, both equipped with liquid nitrogen traps, and then filled with an inert quenching gas. Helium and argon were used at pressures ranging up to 400 torr. Then graphite rods (as previously described herein) were evaporated using a current of about 100 amps (either AC or DC).

The smoke which formed in the vicinity of the evaporating carbon rods was collected on substrates which were placed within 5 cm to 10 cm of the evaporating carbon rods.

15 The evaporator was opened after a cool down period of 10-30 min. and the carbon dust samples removed by scraping substrate surfaces and the internal surfaces of the bell-jar. After washing with ether, the collected dust samples were then extracted with benzene to produce 20 a wine-red to brown solution. On evaporation of the solution, C<sub>60</sub> was obtained as a microcrystalline residue.

The crystals were sublimed by heating <u>in vacuo</u> or in a quenching inert gas to 400°C. and collected on a substrate. The sublimed product was brown to gray in color.

In powder form, the present new carbon allotrope is brownish-red.

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EXAMPLE 2

1 The procedure of Example 1 is repeated except, in the original step, the graphite rods are evaporated at 2 or more atmospheres of helium pressure in the chamber. The product obtained from this procedure contains a greater percentage of  $C_{70}$  than does the product in Example 1.

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EXAMPLE 3

Pure C<sub>60</sub> and pure C<sub>70</sub> are obtained as follows:

The  $C_{60}$  and  $C_{70}$  mixtures prepared in either Examples 1 or 2 are dissolved in benzene and added to an alumina column. Using benzene as the eluent, the fractions are collected and each elute fraction is evaporated to dryness. The presence of  $C_{60}$  or  $C_{70}$  in the fraction can be determined by taking mass spectroscopy thereof.

The above embodiments and examples are given to illustrate the scope and spirit of the instant invention. These embodiments and examples are within the contemplation of the present invention. Therefore, the present invention should be limited only by the appended claims.